



KONGERØET NORGE

The Kingdom of Norway

PCT/NO 03/00135

10/518154

Rec'd PET/PTO 09 DEG 2004

REC'D 15 MAY 2003

WIPO

PCT

Bekrefelse på patentsøknad nr

*Certification of patent application no*

2002 2884

Det bekreftes herved at vedheftede dokument er nøyaktig utskrift/kopi av ovennevnte søknad, som opprinnelig inngitt 2002.06.17

*It is hereby certified that the annexed document is a true copy of the above-mentioned application, as originally filed on 2002.06.17*

2003.04.30

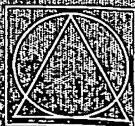
*Freddy Strømmen*

Freddy Strømmen  
Seksjonsleder

**PRIORITY DOCUMENT**  
SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH  
RULE 17.1(a) OR (b)

*Line Reum*

Line Reum



**PATENTSTYRRET®**

Styret for det industrielle rettsvernet



02-06-17\*20022884

C1

## Søknad om patent

Sakars/filmskriftens referanse  
(engels hvilens ønsket):

E 1055.0

Skal utfylles av Patentstyret

Behandlende medlem

UR

CO1B

Silisiumoksid slurry og fremgangsmåte for fremstilling derav.  
Alm. tilgj. 18 DES 2003

Oppfinnelsens  
benevnelse:

Silicon oxide slurry and method for producing such slurry.

Hvis søkeren er  
en internasjonal søknad  
som videreføres etter  
patentlovens § 31:

Den internasjonale søknads nummer .....

Den internasjonale søknads inngivelsesdag .....

**Søker:**  
Navn, adresse  
(Hvis patent søkeres av flere:  
opplysning om hvem som skal  
være berettiget til å motta  
meddelinger fra Patentstyret på  
vognen av søkerne).

(Fortsett om nødvendig på neste side)

Elkem ASA  
Hoffsveien 65B  
0377 Oslo

Søker er en enkeltperson eller en småbedrift, eller flere slike i fellesskap med fast ansatte som til-  
sammen utfører 20 årsverk eller mindre (på søknadstidspunktet). Det er søkers ansvar å krysse av her  
for å oppnå laveste satser for søknadsavgift. NB! se også utfyllende forklaring på siste side.

**Oppfinner:**  
Navn og (privat-) adresse  
(Fortsett om nødvendig på neste side)

1. Bjørn Vassøy, Fagerstølveien 8, 4027 Stavanger
2. Eldar Dingsøy, Tjønneheia 1, 4640 Søgne
3. Magne Dåstøl, Marviksveien 91, 4632 Kristiansand
4. Cor Oldenziel, Taborstraat 12, 3061 EW Rotterdam, Nederland

**Fullmektig:**

Magne Vindenes c/o Elkem ASA Patentavdelingen  
P.O.Box 8040 Vågsbygd  
4675 Kristiansand

Hvis søkeren tidligere  
er inngitt i eller  
utenfor riket:

(Fortsett om nødvendig på neste side)

Prioritet kreves fra dato ..... sted ..... nr. ....

Prioritet kreves fra dato ..... sted ..... nr. ....

Prioritet kreves fra dato ..... sted ..... nr. ....

**Hvis avdelt søkeren:**

Den opprinnelige søkerens nr.: ..... og deres inngivelsesdag .....

**Hvis utskilt søkeren:**

Den opprinnelige søkerens nr.: ..... begjært inngivelsesdag .....

**Deponert kultur av  
mikroorganisme:**

Søknaden omfatter kultur av mikroorganisme. Oppgi også deponeringssted og nr. ....

**Utlevering av prøve av  
kulturen:**

Prøve av den deponerte kultur av mikroorganisme skal bare utleverses til en særlig sakkyndig.  
Jfr. patentlovens § 22 attende ledd og patentforskriftenes § 38 første ledd

**Angivelse av tegnings-  
figur som ønskes  
publisert sammen med  
sammendraget**

Fig. nr. ....

## **Field of invention**

The present invention relates to an additive for oil well cement containing amorphous silica particles and silica flour and to a method for producing such additive

## **5 Background art**

From EP-B 467921 it is known a method for the mixture of silicon dioxide to a hydraulic cement slurry, where amorphous silica with particles smaller than 1 µm is mixed with water to form an aqueous slurry of microsilica whereafter silica flour with particles with a size from 2 – 200 µm are mixed into the suspension of amorphous silica particles. Finally, the produced liquid slurry is added to a cement slurry in a mixing tank.

The cement slurry produced according to the method of EP-B 467921 is particularly useful for cementing oil wells at high temperatures of above 100°C as it has been found that this prevent long time reduction of strength of  
15 the cement.

In order to make full economic and practical use of the method according to EP-B 467921 the slurry containing amorphous silica and silica flour should be produced and transported to the cementing site for mixing to the cement slurry shortly before cementing. For use in cementing of oil wells offshore and on  
20 shore, this means that the slurry of microsilica and silica flour must be produced ashore and transported to a rig before it can be mixed into a cement slurry. Unfortunately it has been found that the suspension of amorphous silica and silica flour shows a strong tendency of settling resulting in such a short shelf life that the suspension cannot be transported for mixing into cement slurries. There is thus a need for a slurry of the type disclosed in EP-B 467921 which have a reduced tendency of settling and which is compatible  
25 with cement slurries.

## **Disclosure of Invention**

By the present invention it has now been provided a slurry of amorphous silica and silica flour and a method for production of such slurry which shows a  
30

strongly reduced tendency of settling and which is compatible with cement slurries and which does not contain any toxic additives.

Thus, according to a first aspect, the present invention relates to a slurry containing water, amorphous silica particles having a particle size less than 1 micrometer and silica flour having a particle size between 2 and 200 µm, which slurry is characterized in that it contains a polysaccharide.

According to a preferred embodiment the polysaccharide is a cellulose derivate selected among xanthan, carboxymethylcellulose, hydroxymethylcellulose, hydroxyethylcellulose or mixtures of these compounds.

According to a further preferred embodiment the slurry contains between 0.01 and 3 grams of polysaccharide pr. litre of slurry and more preferably between 0.05 and 1.5 grams of polysaccharide pr. litre of slurry.

The amount of polysaccharide pr. litre of slurry is adjusted according to the chain length of the polysaccharide. When using polysaccharides having a short chain length, the amount of polysaccharide in the slurry is in the upper end of the ranges and when using polysaccharide having a long chain length the amount is in the lower part of the range.

In order to further increase the stabilizing effect of the polysaccharide, the slurry optionally contains one or more of dextrin, guar gum and locust bean gum.

The slurry according to the invention may contain varying amounts of amorphous silica and silica flour, but the amount of amorphous silica is generally between 15 - 50 % by weight based on the weight of the slurry and the amount of silica flour is generally between 5 and 60 % by weight based on the weight of the slurry.

The total amount of dry matter in the slurry is preferably between 40 and 80 % by weight based on the weight of the slurry.

It has surprisingly been found that the slurry according to the invention is very stable and shows little or no tendency of settling even after two to three months storage. The slurry can thus be stored and transported to the sites where it is mixed into cement slurries. Further it has been found that the slurry  
5 according to the invention is compatible with cement slurries in that it gives an acceptable rheology of the cement slurries.

According to a second embodiment the present invention relates to a method for the production of a slurry containing water, amorphous silica having a particle size below 1 $\mu\text{m}$ , and silica flour having a particle size between 2 and  
10 200  $\mu\text{m}$ , which method is characterized in that a polysaccharide is added to a slurry of water and amorphous silica, whereafter the silica flour is mixed into the slurry of amorphous silica.

According to a preferred embodiment the polysaccharide is preconditioned in a water-containing medium for at least 15 minutes before it is added to the  
15 slurry of water and amorphous silica.

The polysaccharide is preferably preconditioned in a slurry of water and amorphous silica.

According to a preferred embodiment the polysaccharide added to the slurry of amorphous silica and water is a cellulose derivate such xanthan,  
20 carboxymethylcellulose, hydroxymethylcellulose, hydroxyethylcellulose or mixtures of these compounds.

Preferably the silica flour is mixed into the slurry of water and amorphous silica using a high shear energy mixer.

25 The polysaccharide is preferably added to the slurry of amorphous silica and water in an amount necessary to provide a content of polysaccharide in the final slurry of 0.01 to 3 grams pr. litre and more preferably in an amount of 0.05 and 1,5 grams pr litre.

It has surprisingly been found that the addition polysaccharide to the slurry of  
30 amorphous silica and silica flour results in a stable slurry with a strongly

reduced tendency of settling resulting in a strongly increased shelf life of the slurries. The preconditioning of the polysaccharide has shown to even further improve the stability of the final slurry. Further it has been found that the addition of polysaccharides gives acceptable rheological properties for oil well cement slurries containing the slurries according to the invention. Finally polysaccharides are generally non-toxic compounds which are approved to be used in connection with oil well cements.

### Detailed description of the Invention

#### 10 Example 1

0,44 grams of xanthan pr. litre of final slurry was added to a slurry of amorphous silica and water containing 50 % by weight of amorphous silica. The xanthan had been preconditioned in a small part of the slurry of water and amorphous silica for 24 hours before it was added. 850 grams pr litre of final 15 slurry of silica flour having a mean particle size of 25 µm was thereafter added to the slurry using a high shear mixer. The final slurry was stored in 100 ml glass cylinders for 34 days. The samples in the glass cylinders had a 2 mm top layer of water after 34 days, but no resistance was found when lowering a rod to the bottom of the cylinder. The samples were very fluid and when the 20 cylinders were emptied there was not found any settling in the bottom of the cylinders.

For comparison purposes an identical slurry was made, but without the addition of xanthan. After 7 days it was found that excessive settling had occurred. The cylinder had a 25 mm top layer of water and a hard layer was 25 found in the bottom of cylinder which layer could not be redispersed. The hard layer consisted of silica flour.

#### Example 2

A slurry according to the invention was made in the same way as described in Example 1, except that 0.22 grams of hydroxyethylcellulose was added 30 instead of xanthan. The slurry was filled into a glass cylinder. After 1 week

storage the slurry had a 10 mm top layer of water and no hard bottom layer was found.

### Example 3

A slurry according to the invention was made in the same way as described in  
5 Example 1, except that 0.22 grams carboxymethylcellulose was added instead of xanthan. The slurry was filled into a glass cylinder. After 1 week storage the slurry had a 8 mm top layer of water and no hard bottom layer was found.

10 The above examples show that the slurry according to the invention has a strongly reduced settling compared to the prior art slurry.

### Example 4

A slurry of amorphous silica and silica flour containing xanthan according to the present invention and made according to Example 1 was added to an oil well cement slurry in an amount necessary to provide a total SiO<sub>2</sub> content in  
15 the cement slurry of 35 % by weight based on the weight of cement. The slurry had a density of 1.9 g/cm<sup>3</sup>. This slurry is denoted slurry A

For comparison purpose it was made an identical cement slurry B except that cement slurry B was made by adding a slurry of amorphous silica and silica flour that did not contain a polysaccharide additive.

20 The rheological properties of the two cement slurries were measured according to API Specification 10 and the results are shown in Table 1.

**TABLE 1**

Cement slurry	A	B
Rheology (20°C)		
Plastic viscosity, cp	64.5	48
Yield point, lb/100ft <sup>3</sup>	8.5	3
Rheology (88°C)		
Plastic viscosity, cp	45	37.5
Yield point, lb/100ft <sup>3</sup>	6	1.5

5 As can be seen from Table 1, the rheological properties of a cement slurry containing the slurry of amorphous silica and silica flour according to the invention does not deviate much from the same properties of the prior art slurry B and are well within the ranges accepted for oil well cement slurries.



7

**CLAIMS:**

1. Slurry containing water, amorphous silica particles having a particle size less than 1 µm and silica flour with a particle size between 2 – 200 µm, characterized in that the slurry contains a polysaccharide as a stabilizer.
2. Slurry according to claim 1, characterized in that the polysaccharide is a cellulose derivate selected among xanthan, carboxymethylcellulose, hydroxymethylcellulose, hydroxyethylcellulose, and mixtures of these compounds.
3. Slurry according to claim 1, characterized in that the slurry contains between 0.01 and 3 grams of polysaccharide pr. litre of slurry.
4. Slurry according to claim 3, characterized in that the slurry contains between 0.05 and 1.5 grams of polysaccharide pr. litre of slurry.
5. Slurry according to claim 1 – 4, characterized in that the slurry further contains one or more of dextrin, guar gum and locust bean gum.
6. Method for the production of a slurry containing water, amorphous silica having a particle size below 1 µm, and silica flour with a particle size between 2 – 200 µm, characterized in that a polysaccharide is added to a slurry of water and amorphous silica, whereafter the silica flour is mixed into the slurry of amorphous silica.
7. Method according to claim 6, characterized in that the polysaccharide is preconditioned in a water containing medium.
8. Method according to claim 7, characterized in that polysaccharide is preconditioned in a slurry of water and amorphous silica.

9. Method according to claim 6, characterized in that the silica flour is mixed into the slurry of water and amorphous silica using a high shear energy mixer.

10. Method according to claim 6, characterized in that the polysaccharide is added to the slurry of amorphous silica and water in an amount necessary to provide a content of polysaccharide in the final slurry of 0.01 to 3 grams pr. litre.

11. Method according to claim 10, characterized in that the polysaccharide added to the slurry of amorphous silica and water in an amount necessary to provide a content of polysaccharide in the final slurry of 0.1 and 1,5 grams pr litre.

12. Method according to claim 1 -10, characterized in that the polysaccharide added is a cellulose derivate selected among xanthan, carboxymethylcellulose, hydroxymethylcellulose, hydroxyethylcellulose and mixtures of these compounds.



## ABSTRACT

The present invention relates to a slurry containing water, amorphous silica particles having a particle size less than 1  $\mu\text{m}$  and silica flour with a particle size between 2 – 200  $\mu\text{m}$ . In order to stabilize the slurry, the slurry contains a polysaccharide.

The invention further relates to a method for the production of a slurry containing water, amorphous silica having a particle size below 1  $\mu\text{m}$ , and silica flour with a particle size between 2 – 200  $\mu\text{m}$ , where a polysaccharide is added to a slurry of water and amorphous silica, whereafter the silica flour is mixed into the slurry of amorphous silica.

